*Proceeding Paper*

# Effect of Potassium Formate on Alkali–Silica Reaction in Aggregates with Different Categories of Reactivity †

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**Abstract:** During the wintertime, concrete pavements experience harsh exposure conditions due to the presence of both the freezing–thawing and wetting–drying cycles. Airport concrete pavements are commonly de-iced using chloride-free organic salts such as potassium formate or potassium acetate. However, these materials contain alkali ions which can have harmful effects on both the cement matrix and the aggregate. Specifically, there is an increased risk of occurrence of the alkali–silica reaction (ASR). The goal of this research was to estimate the influence of potassium formate on the potential of causing alkali–silica reaction in aggregates with different categories of reactivity (R0, R1, R2). The accelerated mortar bar test and its modification (which involves replacing sodium hydroxide solution with a potassium formate solution) were used. Detailed SEM-EDS examinations were performed to confirm the presence of alkali–silica reaction and to analyze the influence of potassium formate on the microstructure of mortar.

**Keywords:** alkali–silica reaction; potassium formate; de-icing agent; reactive aggregate

## 1. Introduction

The alkali–silica reaction (ASR) is a chemical reaction between the alkali and hydroxyl ions present in the concrete pore solution and certain reactive forms of silica present in the aggregate [1]. This phenomenon is characterized by formation of an alkali–silica gel that absorbs water and expands, ultimately causing cracks in the aggregate and then in the cement matrix [2]. Although the predominant source of alkalis in concrete is Portland cement, other sources of alkalis, such as de-icing salts or agents, have been shown to contribute to ASR in concrete, [3–5].

Chloride based de-icers ($NaCl$, $MgCl_2$ and $CaCl_2$) are the most common de-icing salts used during winter months to clean the concrete road pavement and enable a normal flow of traffic [6]. However, they may have detrimental effects on concrete durability, which is often manifested by expansion, mass change, reduction in the dynamic modulus of elasticity [1] and, most of all, reduction in strength [5]. At the same time, due to the risk of aircraft corrosion, their use on airfield pavements is not allowed. Alternative agents used for de-icing airport pavements include sodium and potassium formates or acetates [7].

Studies on the effects of formate- and acetate-based de-icing agents have already been published, [3,4,8]. Wang et al. [3] analyzed the influence of de-icing agents on concrete degradation due to ASR. They used potassium acetate, which has a similar effect to potassium formate. The authors did not observe significant damage in the macro- or micro-scale and they did not find ASR products, despite using a high concentration of potassium acetate (54.4 wt. %). On the other hand, Rangaraju et al. [8] found that the two common airfield de-icing chemicals—potassium acetate and sodium acetate-based de-icer solutions—have significant potential to cause ASR in test specimens containing reactive aggregates. The research conducted by Giebson et al. [4] came to similar conclusions. They

revealed that deleterious ASR can be initiated and accelerated in concretes with reactive aggregates exposed to alkali-containing de-icers, especially ones based on acetates and formates. They showed that even low-alkali cement was not able to prevent the ASR.

Real-life experience shows that even in concrete made of nominally non-reactive aggregates, ASR can sometimes occur under adverse conditions of additional external alkali supply, humid environment, or heavy traffic and load [9]. The goal of the current research was to determine the impact of potassium formate on the potential for the occurrence of ASR in aggregates with different levels of reactivity.

## 2. Materials

Three aggregates characterized by different categories of reactivity were selected for testing. ASR reactivity was tested according to PB/1/18 [10], which is based on expansion measurements. Two granite aggregates (G1, G2) and one quartzite aggregate (Q) met the initial requirements of the research regarding the ASR reactivity category; they were R0—non-reactive (G2), R1—moderately reactive (G1), and R2—highly reactive (Q). The category of reactivity of aggregate according to PB/1/18 is presented in Table 1.

**Table 1.** Category of ASR reactivity according to PB/1/18 [10].

| Category of ASR Reactivity | Reactivity | 14-Day Expansion [%] |
|---|---|---|
| R0 | Non-reactive | $\leq 0.10$ |
| R1 | Moderately reactive | $>0.10; \leq 0.30$ |
| R2 | Highly reactive | $>0.30; \leq 0.45$ |
| R3 | Very highly reactive | $>0.45$ |

Ordinary Portland cement CEM I 42.5 R was used for mortar specimens. The alkali content in cement was 0.86%.
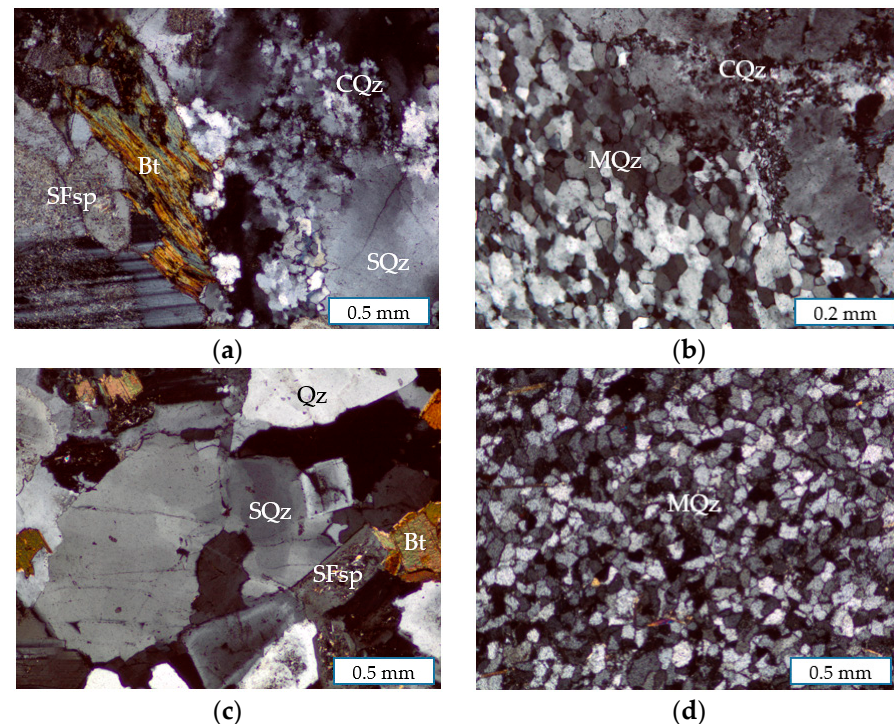
## 3. Methods

Aggregate for petrographic analysis was prepared according to Technical Guidelines [11]. The identification of reactive minerals presented in tested aggregates was conducted on thin sections of $30 \pm 1$ μm thickness. Polarizing microscope Olympus BX51 equipped with a digital colour camera and an automatic stage Prior ES11BX/B was used for petrographic observations. Transmitted light with parallel (PPL) and crossed (XPL) polarizers was used.

The expansion tests of mortars were performed according to the accelerated mortar bar test described in PB/1/18 [9]. The above method is similar to the one given in the ASTM C 1260 [12]. The specimens ($25 \times 25 \times 285$ mm) were exposed to 1 M NaOH and 80 °C for 28 days. The method was modified using de-icing agent (50% concentration of potassium formate (HCOOK)) as a soak solution. The Federal Aviation Administration Advisory Circular: Standard Specifications for Construction of Airports concerning cement concrete pavement [13] stipulates that alkali–silica reactivity of the aggregates used in Portland cement concrete pavements shall be tested and evaluated using the modified ASTM C1260 [12], among other guidelines. The modification of the testing method involves extending the length of the test from 14 to 28 days.

After the accelerated mortar bar test, the specimens were cut ($40 \times 25 \times 10$ mm) and prepared for post-mortem microscopic observations. The specimens were dried, impregnated with epoxy resin, ground on diamond discs (125, 75, 54, 18 and 9 μm), and polished on polishing pads using diamond pastes (6, 3, 1, 0.25 μm). Then, specimens were coated with a thin carbon layer. Microstructure analysis was performed on a JEOL JSM-6460LV scanning electron microscope (SEM) equipped with an X-ray energy dispersion (EDS) detector. The analysis was performed at high vacuum in the backscattered electron mode. The SEM was operated with acceleration voltage set to 20 kV and a working distance of 10 mm.

## 4. Results and Discussion

In the first step, the petrographic analysis was performed on thin sections. The aggregate was analyzed for the presence of reactive minerals (Figure 1). A significant presence of microcrystalline quartz was found in granite aggregate G1 and quartzite aggregate Q. Microcrystalline quartz was not found in the granite G2 sample, but strained quartz was found.
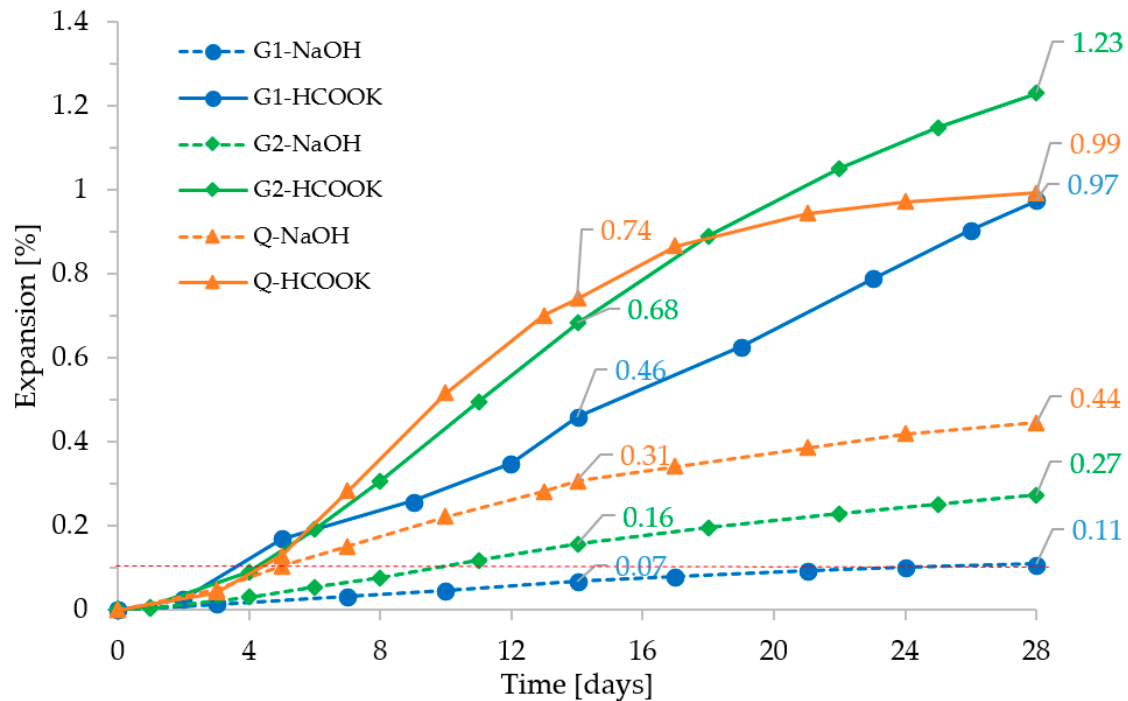


**Figure 1.** The microphotographs of the analyzed aggregates in cross-polarized light (XPL) (**a,b**) granite G1 aggregate, (**c**) granite G2 aggregate, (**d**) quartzite Q, aggregate; recognized minerals: Qz—quartz, SQz—strained quartz, MQz—microcrystalline quartz, CQz—cryptocrystalline quartz, SFsp—feldspar alteration to sericite, Bt—biotite.

Expansion of mortar bars over a 28-day period is presented on Figure 2. The expansion of mortar bars exposed to 1 M NaOH after 14 days confirmed the aggregate reactivity categories. Granite aggregate G1 characterized by 0.07% expansion was classified as the R0 category, granite G2 with 0.16% expansion as the R1 category, and quartzite with 0.31% expansion as the R2 category. Extending the PB/1/18 [10] to 28 days did not significantly slow down the rate of expansion.

Mortar bars stored in potassium formate solution expanded significantly more than those stored in sodium hydroxide solution. In the case of granite aggregates, expansion was found to increase at a constant rate for 28 days, without a significant slowdown. However, a slowdown in the expansion of mortar bars with quartzite aggregate was observed after 17 days of storage in a potassium formate solution. After 28 days of storage in 50% HCOOK, the following expansion values were found: G1—0.97%, G2—1.23%, Q—0.99%. The expansion of mortars with G1 and Q aggregates was similar after 28 days of storage in HCOOK, although in the sodium hydroxide solution, the mortar with the G1 aggregate had four times lower expansion than the mortar with the Q aggregate. The slowdown of the reaction in the case of quartzite aggregate may be related to the presence of reactive minerals in the form of micro- and cryptocrystalline quartz, which are fast-reacting minerals. In the first few days of the test, the highest increase in expansion among all the tested aggregates is visible. However, as a result of the exhaustion of reactive components, the rate of further increase in expansion decreases. However, in specimens with granite
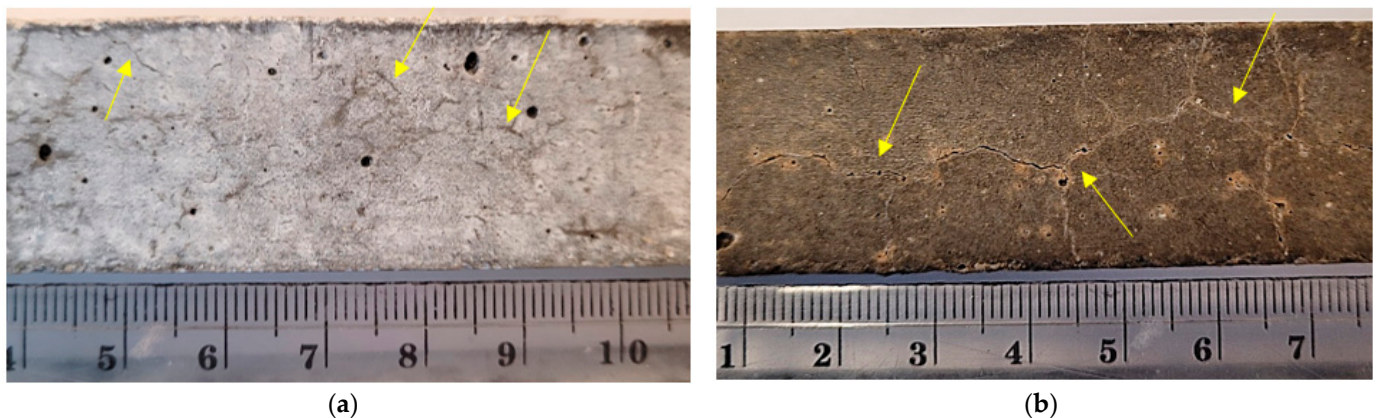
aggregate (G1, G2), apart from micro- and cryptocrystalline quartz, we also discovered strained quartz, which is classified as a slowly reacting mineral [14–16]. The reaction was not slowed down due to the presence of both fast and slow reacting minerals.
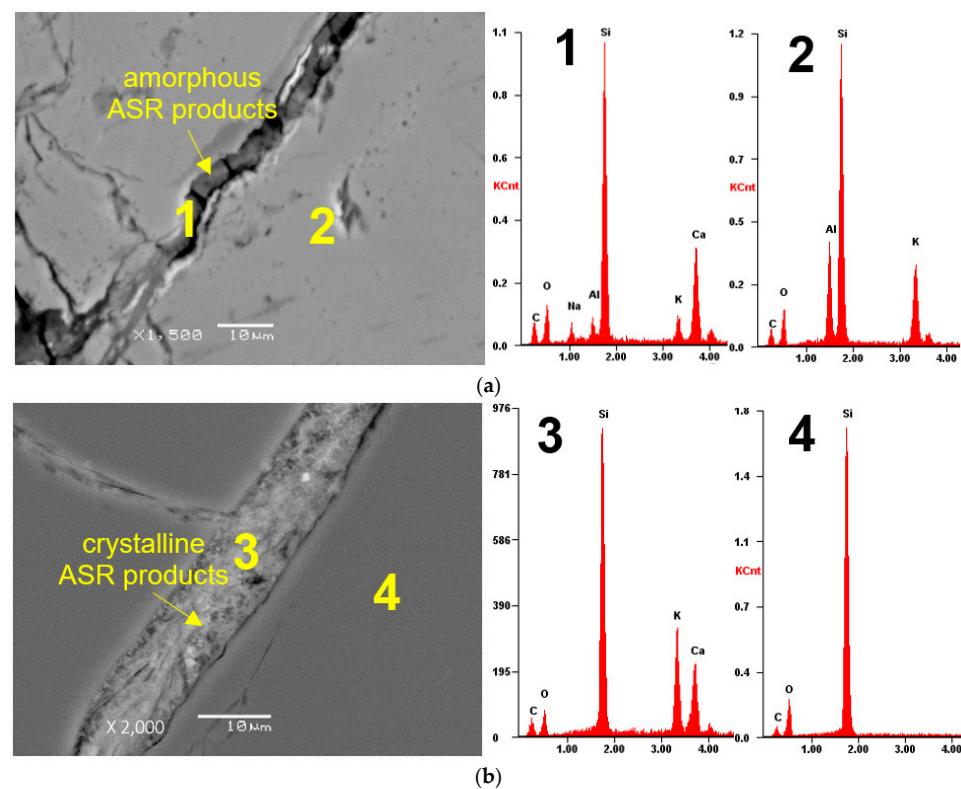


**Figure 2.** Expansion of mortar bars with aggregate with different ASR reactivity (R0, R1, R2) exposed to 1 M NaOH or 50% HCOOK solution.

Cracks were observed on the surface of all mortar specimens. Larger cracks were seen in mortar bars stored in potassium formate solution (Figure 3).
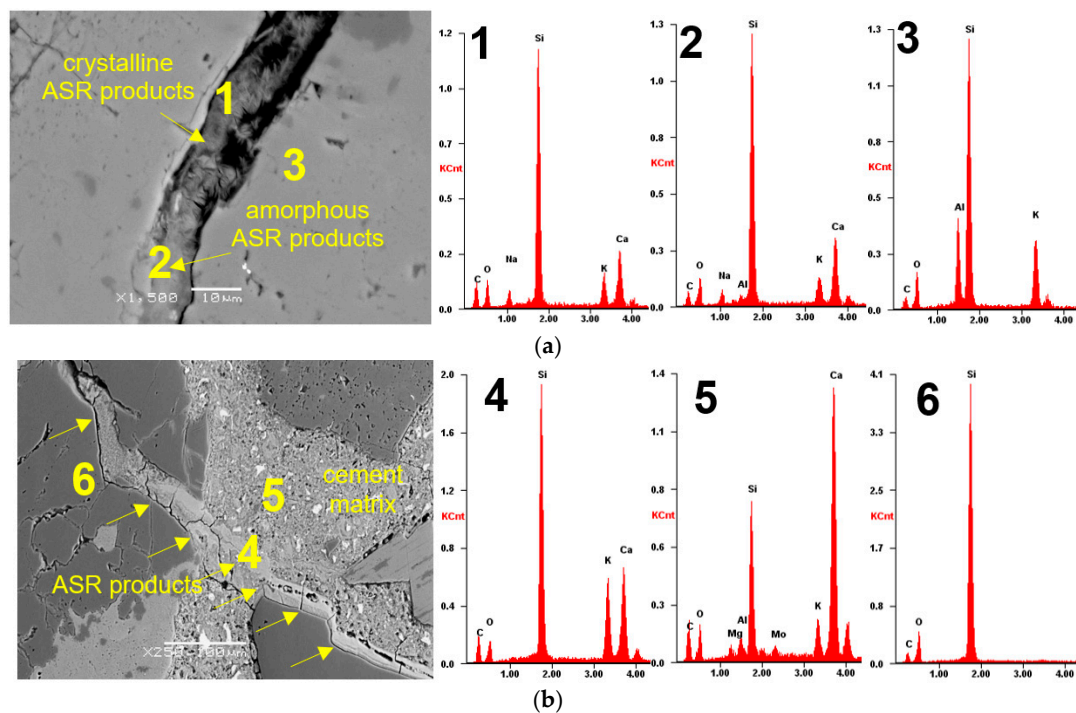


**Figure 3.** Cracks on the surface of mortar bars with quartzite Q aggregate immersed in (**a**) 1 M NaOH, (**b**) 50% HCOOK.
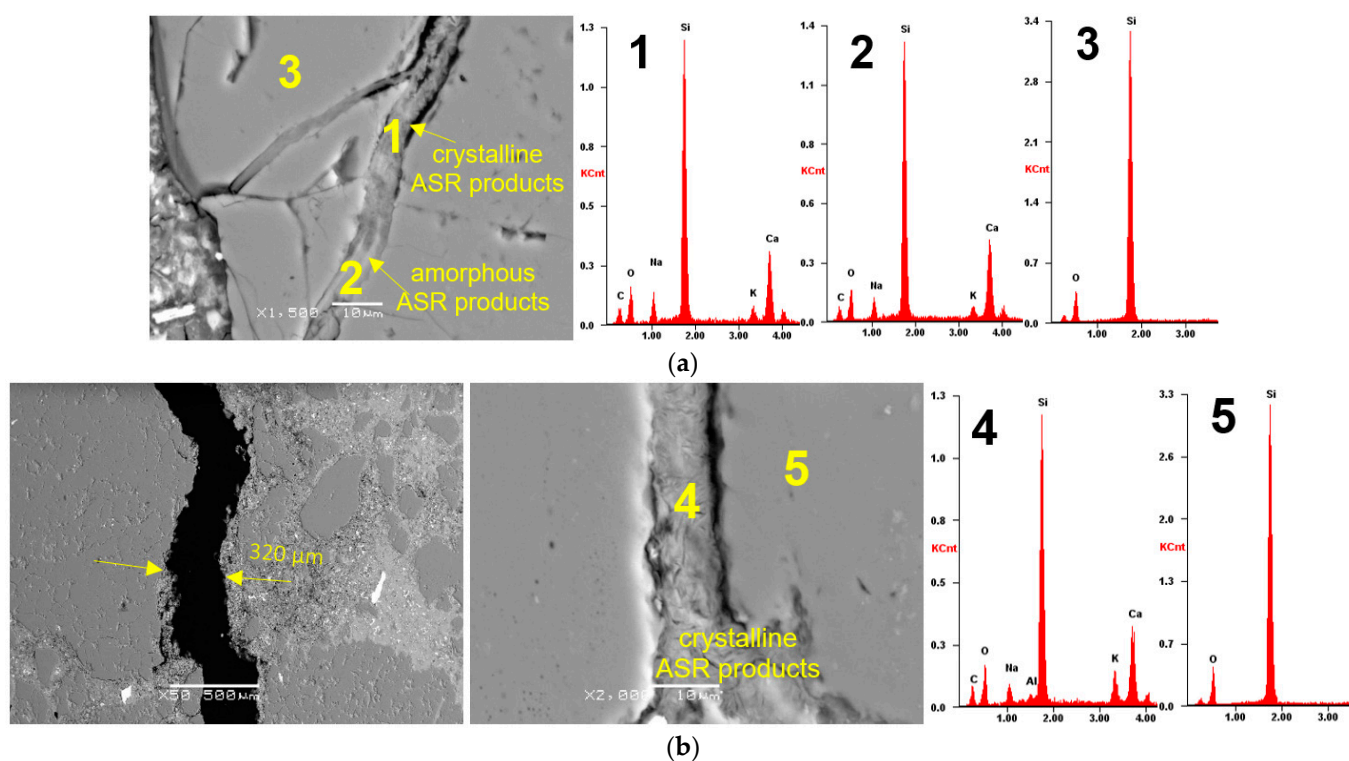
For a more detailed analysis, microscopic examinations were carried out on polished specimens using SEM. Results are presented in Figures 4–6.

**Figure 4.** Microstructure of the mortar with aggregate G1 after 28 days of storage at 80 °C in (**a**) 1 M NaOH, crack in the aggregate grain filled with amorphous ASR products (1), potassium feldspar (2); (**b**) 50% HCOOK, crack in the aggregate grain filled with crystalline ASR products (3), quartz (4).



**Figure 5.** Microstructure of the mortar with aggregate G2 after 28 days of storage at 80 °C in (**a**) 1 M NaOH, crack in the aggregate grain filled with crystalline (1) and amorphous (2) ASR products, (3) potassium feldspar; (**b**) 50% HCOOK, crack in the aggregate grain filled with ASR products that penetrates the cement matric (5), C-S-H (5), quartz (6).

**Figure 6.** Microstructure of the mortar with aggregate Q after 28 days of storage at 80 °C in (**a**) 1 M NaOH, cracks in the aggregate grain filled with crystalline (1) and amorphous (2) ASR products; (**b**) 50% HCOOK, crack of 320 μm and crack in the aggregate grain filled with crystalline ASR products (4), quartz (5).

The presence of ASR products was found in all analyzed mortar bars. The identified reaction products were found in both crystalline and amorphous forms (distinguished by morphology). The ASR products were mainly found in the cracks of the aggregate grains, but also in the cement matrix (Figure 5b). Large macro-cracks were observed in the specimens stored in potassium formate solution. Their width was between 100 and 500 μm. The chemical composition of the ASR products identified in the aggregate varied depending on the storage solution (NaOH, HCOOH). There was no significant influence of the type of aggregate (granite, quartzite) on chemical composition in the reaction products. In the ASR gel found in mortar bars after storage in NaOH solution, the values of the Ca/Si and (Na+K)/Si were 0.25–0.35 and 0.20–0.25, respectively. However, the ASR products in the mortar bars stored in the HCOOK solution were characterized by Ca/Si and (Na+K)/Si of 0.3–0.45 and 0.25–0.35, respectively (alkali was present only in the form of potassium).

The obtained test results are in line with expectations. Sodium salts of acetate and formate have a significant potential to exert detrimental effects on concretes, causing deleterious ASR in mortar and concrete specimens containing reactive aggregates [17]. However, the deleterious ASR symptoms were not seen in specimens containing non-reactive aggregate [18]. The conducted research showed the effect of potassium formate on the potential for ASR occurrence in aggregate of various reactivity categories. Leeman et al. [19] analyzed crystalline and amorphous ASR products. The chemical composition of the ASR gel was similar to the results obtained in the conducted research, but only for the specimens tested in 1 M NaOH solution. For amorphous and crystalline ASR products, Ca/Si 0.21–0.23 and 0.22–0.26, respectively, (Na+K)/Si: 0.21–0.24 and 0.22–0.34, respectively.

The next stage of research will concern the impact of de-icing chemicals based on the formates on real concrete mixes used in airport concrete pavements as well as more accurate characterization of ASR products using Transmission Electron Microscopy, Raman spectroscopy and nanoindentation techniques.

## 5. Conclusions

Based on the conducted research, the following conclusions can be drawn:

- The presence of reactive minerals: micro- and cryptocrystalline quartz was found in the quartzite and granite aggregate. In addition, strained quartz was present in one granite aggregate.
- The accelerated mortar bar test confirmed different categories of reactivity of the tested aggregate.
- Regardless of the aggregate reactivity category, the mortar bars stored in the 50% potassium formate solution reached very high expansion values, including granite G1 with the R0 reactivity category.
- Reduction in the expansion rate of quartzite aggregate in potassium formate solution was probably associated with the depletion of fast-reacting minerals (micro- and cryptocrystalline quartz). Such phenomena were not observed in mortars with granite aggregate, in which strained quartz (a slow-reacting mineral) was the main reactive mineral.
- The presence of ASR products was found in all analyzed mortar bar specimens.
- The chemical composition of the gel varied depending on the mortar storage solution (NaOH, HCOOK). The gel identified in the cracks of aggregate grains in the mortar in the potassium formate solution was characterized by a higher alkali content, specifically potassium.

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